Organosilicon and organotin derivatives of triruthenium carbonyl cluster complexes

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1. INTRODUCTION

The reactions of organosilanes with unsaturated organic substrates are always catalysed by transition metal compounds. These reactions have now become very important in organic synthesis (Ojima 1989, Marciniec 1992); in fact, some of them are of considerable interest in connection with industrial processes (Noels & Hubert 1988).

![Image](image)

In this context, as far as ruthenium carbonyl cluster complexes are concerned, \([\text{Ru}_3(\text{CO})_{12}]^{-}\) (1) has demonstrated to be an efficient homogeneous catalyst precursor for alkene hydroformylation (Tanaka et al. 1993, Hilal et al. 1993) and for the selective reaction of alkenes with triorganosilanes to give vinylsilanes (Ojima et al. 1984, Seki et al. 1980 and 1986, Kakuchi et al. 1993). On the other hand, the cluster anion \([\text{Ru}_3(\mu-\text{H})(\mu-\text{CO})(\text{CO})_{10}]^{-}\) (2) has been found to promote the coupling of silanes with \(\text{CO}_2\) to give silyl formates (Süss-Fink & Reiner 1981), the reaction of ethylene with \(\text{CO}\) and \(\text{HSiEt}_3\) to give unsaturated silyl ethers (Süss-Fink 1983), and the spirocyclisation of isocyanates in the presence of \(\text{HSiEt}_3\) (Herrmann & Süss-Fink 1985).

![Image](image)

In contrast with the interesting catalytic activity commented above, very little is known about the mechanisms operating in these reactions or about the nuclearity of the actual catalytic species. Therefore, the more we know about the reactivity of ruthenium carbonyl clusters with silanes, the more light can be shed on the catalytic reaction mechanisms involving these reagents.

Although the reactions of organostannanes with unsaturated organic substrates are not metal-catalysed (Pereyre et al. 1986, Stille 1986), the reactivity of transition metal complexes with organostannanes (Holt et al. 1989) and organosilanes (Schubert 1990) can be compared in many aspects. Therefore, the synthesis, structure and reactivity of ruthenium carbonyl cluster complexes containing triorganostannyl ligands may be relevant to the chemistry of ruthenium carbonyl clusters containing triorganosilyl ligands.

This article reviews the reactivity of triruthenium carbonyl cluster complexes with triorganosilanes and triorganostannanes. The survey, which is classified according to the type of ruthenium cluster which reacts with triorganosilanes and triorganostannanes, covers the literature published up to the end of 1993 and is followed by a general discussion on the subject.

2. SURVEY OF REACTIONS ARRANGED BY TYPE OF RUTHENIUM CARBONYL CLUSTER

2.1. \([\text{Ru}_3(\text{CO})_{12}]^{-}\)

Trirutheniumdodecacarbonyl (1) reacts with tertiary silanes in hexane under thermal or photochemical conditions to give the binuclear derivatives \([\text{Ru}_2(\text{SiR}_3)_2(\text{CO})_8]^{-}\) (3) in high yield (Cotton et al. 1967, Knox & Stone 1969). Complexes of type 3 have been obtained using \(\text{HSiMe}_3\), \(\text{HSiEt}_3\), \(\text{HSiPr}_3\), \(\text{HSiCl}_3\) or \(\text{HSiMeCl}_2\). From \(\text{HSiPh}_3\) and \(\text{HSi}(\text{OMe})_3\) only spectroscopic identification of the corresponding products was obtained. The reaction of \([\text{Ru}_3(\text{CO})_{12}]^{-}\)
with HSiMe$_3$ also gives a low yield (0-1% under thermal conditions or 10% under photochemical conditions) of the mononuclear compound [Ru(SiMe$_3$)$_2$(CO)$_4$] (4, ER$_3$ = SiMe$_3$).

\[
\begin{align*}
\text{(3)} & \quad [\text{Ru}(\text{SiMe}_3)_2] \quad \text{Ru} \quad [\text{Ru}(\text{SiMe}_3)_2] \\
\text{(4)} & \quad [\text{Ru}(\text{SiMe}_3)_2] \quad \text{ER}_3 \quad [\text{Ru}(\text{SiMe}_3)_2]
\end{align*}
\]

It is interesting to note that similar reactions of [Ru$_3$(CO)$_4$] with tertiary stannanes HSnR$_3$ (R = Me, Et, Pr, Bu, Ph, PhCH$_2$) do not afford binuclear ruthenium(II) complexes analogous to 3, but mononuclear ruthenium(II) derivatives, analogous to 4 (E = Sn), in yields of 60-70%. Small amounts (ca. 3%) of the binuclear ruthenium(III) complexes [Ru$_2$(μ-SnR$_3$)$_2$(SnR)$_3$(CO)$_4$] (5, R = Me, Bu) are also produced in these reactions (Cotton et al. 1968). The compound [Ru$_4$(μ-SnMe$_3$)$_2$(SnMe)$_3$(CO)$_4$] has been characterized by X-ray diffraction methods (Watkins 1969).

\[
\begin{align*}
\text{(5)} & \quad [\text{Ru}(\text{SnMe}_3)_2] \quad \text{Sn} \quad [\text{Ru}(\text{SnMe}_3)_2] \\
\text{(6)} & \quad [\text{Ru}(\text{MeSi}_2)_2] \quad \text{Sn} \quad [\text{Ru}(\text{MeSi}_2)_2]
\end{align*}
\]

The disilane HMe$_2$SiCH$_2$CH$_2$SiMe$_2$H reacts with [Ru$_3$(CO)$_4$] in hexane, under CO at 175 °C, to give [Ru(SiMe$_4$)$_2$H$_2$(CO)]$_2$ (6) in 89% yield (Vancea & Graham 1974).

The trinuclear cluster complexes [Ru$_3$(μ-H)$_3$(SiRC$_2$)$_2$(CO)$_8$] (7, R = Cl, Me) have been isolated, in ca. 50% yield (after a sublimation work up), from the reaction of the appropriate silane with [Ru$_3$(CO)$_4$]$_2$ in hexane at 70 °C. Mononuclear [Ru(SiRC$_2$)$_2$(CO)$_4$] (4) and binuclear [Ru$_2$(SiRC$_2$)$_2$(CO)$_8$] (3) are the by-products of these reactions (Van Buuren et al. 1981).

\[
\begin{align*}
\text{(7)} & \quad [\text{Ru}(\text{SiClR}_2)_2] \quad \text{Cl} \quad [\text{Ru}(\text{SiClR}_2)_2] \\
\text{(8)} & \quad [\text{Ru}(\text{ClSiR}_2)_2] \quad \text{H} \quad [\text{Ru}(\text{ClSiR}_2)_2]
\end{align*}
\]

2.2. [Ru$_3$(CO)$_4$]$_2$(MeCN)

The “activated” cluster [Ru$_3$(CO)$_4$]$_2$(MeCN) (8) (Foulds et al. 1985) reacts with HSnPh$_3$, releasing acetonitrile under very mild conditions (~40 °C, 2 h), to give the trinuclear hydride [Ru$_3$(μ-H)(SnPh$_3$)(CO)$_3$] (9) in 60% yield (Burgess et al. 1985). It is curious that the reaction of [Ru$_3$(CO)$_4$](MeCN) with tertiary silanes does not seem to have been reported.

\[
\begin{align*}
\text{(8)} & \quad [\text{Ru}(\text{MeSi}_2)_2] \quad \text{NCMe} \quad [\text{Ru}(\text{MeSi}_2)_2] \\
\text{(9)} & \quad [\text{Ru}(\text{MeSi}_2)_2] \quad \text{SnPh}_3 \quad [\text{Ru}(\text{MeSi}_2)_2]
\end{align*}
\]

2.3. [Ru$_3$(μ-H)(μ-CO)(CO)$_8$]$_2$ (10)

The reaction of Na[Ru$_3$(μ-H)(μ-CO)(CO)$_8$] (2) (Johnson et al. 1979) with triorganosilanes and triorganostannanes (THF, 45 °C, 4 h) affords trinuclear cluster anions of the type [Ru$_3$(μ-H)(ER)$_3$(CO)$_8$] (10, ER$_3$ = SiPh$_3$, SiEt$_3$, SiPh$_2$Me, SiEt$_2$Me, SnPh$_3$), which can be isolated as [PPN]$^+$ salts (Süss-Fink, Ott et al. 1982). The reactions proceed via elimination of CO and H$_2$, the formation of [Ru$_3$(μ-H)(SiEt$_3$)$_3$(CO)$_8$] from [Ru$_3$(μ-D)(μ-CO)(CO)$_8$] and HSiEt$_3$ indicates that the eliminated hydrogen arises from the cluster. Although two HER$_3$ molecules have to be sequentially incorporated into the cluster, no intermediates containing only one ER$_3$ fragment were detected.

\[
\begin{align*}
\text{(10)} & \quad [\text{Ru}(\text{SiEt}_3)_3] \quad \text{Ru} \quad \text{ER}_3 \quad [\text{Ru}(\text{SiEt}_3)_3]
\end{align*}
\]

The triethylsilyl derivative [PPN][Ru$_3$(μ-H)(SiEt)$_3$(CO)$_8$] (10, ER$_3$ = SiEt$_3$) has been studied by X-ray crystallographic, NMR spectroscopic, and electrochemical methods (Klein et al. 1985). In the solid state, the triethylsilyl groups occupy equatorial sites cis to the bridging hydride ligand, which spans the longest Ru-Ru edge. In solution, only the four carbonyl groups at the unbridged Ru atom are fluxional. At a platinum electrode, the anion can be oxidized to a neutral species, the lifetime of which in dichloromethane is long enough to allow the observation of electrochemical reversibility at a scan rate of 1 V s$^{-1}$. 
2.4. [Ru₃(µ-pydz)(µ-CO)₃(CO)₇]

The edge-bridged trinuclear compound [Ru₃(µ-pydz)(µ-CO)₃(CO)₇] (11, pydz = pyridazine) (Cotton & Jamerson 1976, Cotton et al. 1977) react with excess of tertiary silanes and stannanes in refluxing THF to give the trinuclear derivatives [Ru₃(µ-H)₂(ER₃)₂(µ-pydz)(CO)₈] (12, ER₃ = SiEt₃, SiPh₃, Si(OMe)₃; 13, ER₃ = SnBu₃, SnPh₃) in yields which range from 25 to 54% (Cabeza, Franco, et al. 1993). IR monitoring of the reactions indicated that at least 2 equivalents of tertiary silane or stannane are needed to consume 1 equivalent of complex 11.

From NMR data, it was concluded that the silyl derivatives 12 are asymmetric, whereas the stannyl derivatives 13 are symmetric, with the SnR₃ groups cis to the hydrides. The asymmetric structure of [Ru₃(µ-H)₂(SiEt₃)₂(µ-pydz)(CO)₈] has been confirmed by an X-ray diffraction study (Cabeza, Franco, et al. 1993).

2.5. [Ru₃(µ-H)(µ₃-ampy)(CO)₉]ₙ(PPh₃)ₙ (n = 0-2)

The face-bridged trinuclear complex [Ru₃(µ-H)(µ₃-ampy)(CO)₉] (14, ampy = 2-amino-6-methylpyridinate) (Andreu, Cabeza, Riera, Jeannin & Miguel 1990) and its triphenylphosphine-substituted derivatives [Ru₃(µ-H)(µ₃-ampy)(CO)₈(PPh₃)] (15) (Andreu, Cabeza, Riera, Bois & Jeannin 1990) and [Ru₃(µ-H)(µ₃-ampy)(CO)₇(PPh₃)₂] (16) (Andreu et al. 1991) react with tertiary silanes (HSiEt₃, HSiPh₃, HSi(OMe)₃) and stannanes (HSnBu₃, HSnPh₃), under mild conditions, to give the dihydride derivatives [Ru₃(µ-H)₂(µ₃-ampy)(ER₃)(CO)₈] (n = 0 (17), 1 (18), 2 (19); ER₃ = Si (a), Sn (b)) (see Schemes 1 and 2) (Cabeza, Llamazares, et al. 1992). In all these reactions only 1 equivalent of HER₃ was incorporated into the clusters, even using a large excess of these reagents. In contrast with the results commented above for [Ru₃(µ-pydz)(µ-CO)₃(CO)₇] (11), in this case, the silyl and the stannyl derivatives are isosstructural (IR, NMR). The structure of [Ru₃(µ-H)₂(µ₃-
The reaction of diphenylacetylene with 17a (R = Et) is solvent dependent. In THF it gives the alkynyl complex \([\text{Ru}_3(\mu_3-\text{ampy})(\mu-H)\text{SnR}_3] (17b)\) and HSiEt_3, whereas a mixture of 20 (35%), 21a (49%), and 22a (16%) (R = Et) is observed when the reaction is carried out in toluene. It is interesting to point out that these reactions differ from that of diphenylacetylene with the methoxysilane derivative 17a (R = OMe), since the latter is not solvent dependent and gives a mixture of the isomeric clusters 22a (20%) and 23a (80%) (R = OMe). All these mixtures can be separated by chromatographic methods (Cabeza, García-Granda, et al. 1993).

Diphenylacetylene reacts with the phosphine-substituted complex 18a (R = Et) in refluxing 1.2 dichloroethane to give a mixture of products (complexes 15, 24, and 25) were observed in the NMR spectra of...
the reaction mixture) from which the alkenylsilyl derivative 25 was separated, isolated in 32% yield, and crystallographically characterized. On the other hand, compound 25 is the only product of the reaction of complex 24 with HSiEt$_3$ (Cabeza, García-Granda, et al. 1993).

$$\text{Ru}_3\text{(CO)}_{12}$$

The behavior of the stannyl complexes 17b (R = Bu, Ph) in their reaction with diphenylacetylene parallels that of the above commented trimethoxysilyl derivative 17a (R = OMe), rendering a mixture of the isomeric clusters 22b (25 and ca. 0%) and 23b (75 and ca. 100% for R = Bu and Ph, respectively). Both have been crystallographically characterized for R = Ph (Cabeza, García-Granda, et al. 1993).

2.6. $[\text{Ru}_3(μ-ampy)(μ-Ph_2C=H)(μ-CO)_{12}]$

The alkenyl compound $[\text{Ru}_3(μ-ampy)(μ-Ph_2C=H)(μ-CO)_{12}]$ (20), which is the product of the reaction of complex 14 with diphenylacetylene (Cabeza, Fernández-Colinas, et al. 1992), also reacts with excess of tertiary silanes and stannanes but, again, no hydrosilylated or hydrostannated products were observed (Cabeza, García-Granda, et al. 1993). In all cases (HSiEt$_3$, HSi(OEt)$_3$, HSnBu$_3$, and HSnPh$_2$), the products were a mixture of complexes 17, 21, and 22 (each containing the appropriate Er$_3$ groups).

It should be noted that although the cluster complexes 14 and 15 react with silanes (or stannanes) and diphenylacetylene to form compounds in which SiR$_3$ (or SnR$_3$) groups coexist in the ligand shell of the clusters, they do not promote the hydrosilylation (or hydrostannation) of diphenylacetylene because, among other possible reasons, in all cases, the products have the SiR$_3$ (or SnR$_3$) and diphenylalkenyl ligands attached to different ruthenium atoms: a cis arrangement of both ligands on the same metallic atom is required for the reductive elimination of the hydrosilylated (or hydrostannated) product.

3. GENERAL COMMENTS

As can be observed in the previous section, the amount of work carried out so far on the chemistry of ruthenium carbonyl cluster complexes with tertiary silanes and stannanes is still very small, being restricted to only a few triruthenium complexes. Such limited data do not allow to draw many conclusions.

However, it seems clear that, upon reaction with tertiary silanes and stannanes, cluster fragmentation can be prevented by using starting materials such as (a) "activated" clusters containing weakly bound ligands, or (b) ligand bridged (μ$_2$ or μ$_3$) derivatives. In the former case, i.e. with $[\text{Ru}_3(μ-CO)_{12}]$ (MeCN), the reactions proceed under much milder conditions than those required by $[\text{Ru}_3(μ-CO)_{12}]$. In the latter case, i.e. with $[\text{Ru}_3(μ-H)(μ-ampy)(μ-CO)_{12}]$, fragmentation is impeded by the presence of the bridging ligand and, moreover, the reactions require milder conditions than with $[\text{Ru}_3(μ-CO)_{12}]$ due to the cis-labilizing effect of the N-donor ligands.

As far as the compared reactivity of tertiary silanes and tertiary stannanes is concerned, it seems that the latter are slightly more reactive than the former, requiring milder reaction conditions. This agrees with the observed fact that the reductive elimination of HSiR$_3$ from a hydridosilyl cluster is easier than that of HSnR$_3$ from a hydridostannyl cluster. However, more experimental work and also theoretical calculations are needed to rationalize the behavior of these two types of reagents, which is very similar in some cases and completely different in others.

From a catalytic point of view, no efforts have been devoted to characterize the catalytic species involved in hydrosilylation reactions promoted by ruthenium carbonyl cluster complexes and, with the exception of the hydrosilylation of 1-octene and acetophenone promoted by $[\text{Ru}_3(μ-CO)_{12}]$, in which cluster fragmentation is suggested (Hilal et al. 1993), no kinetic analyses of catalytic reactions have been reported.

Therefore, much more work is needed on this organometallic area.

4. ACKNOWLEDGEMENTS

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5. REFERENCES

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